

REMARKS

This paper is submitted in response to the Office Action for the above-identified application mailed June 26, 2003.

In the Office Action, Claims 10-12 and 14-16 were rejected under 35 U.S.C. Sec. 103 for being obvious over Miyazaki (U.S. Pat. No. 5,689,114) in view of Burch (U.S. Pat. No. 3,916,195). Claim 13 was rejected for being obvious over the above combination further in view of Hagen (German Pat. Pub. No. DE 34 37 397/U.S. Pat. No. 4,644,141)¹. Claim 17 was rejected for being obvious over Miyazaki and Burch further in view of Peters (U.S. Pat. No. 5,550,375). Claim 18 was rejected over Miyazaki and Burch further in view of Hirayama (German Pat. Pub. No. DE 198 08 128/U.S. Patent No. 6,121,617)².

Before discussing this Office Action, the Applicants call to the attention of the Examiner one minor issue with regard to the Information Disclosure Statement filed coincidentally with the filing of this application. Under cover of this paper, the Applicants requested the Examiner acknowledge considering the documents cited by the European Patent Office in its review of the underlying Patent Cooperation Treaty application upon which this application is based. According to the 371 Acceptance Letter mailed for this application on October 29, 2001, the Patent and Trademark Office received the documents cited in the International Search Report generated by the European Patent Office.

One of the cited documents was U.S. Patent No. 5,876,674 to Dosoretz. Unfortunately this document was slightly mis-identified on the Form-1449. The Applicants now provide a new Form 1449 with the document properly identified. The Applicants courteously request that the Examiner now

¹ In the Office Action, only the '397 DE Patent Publication was cited. The '141 US Patent is an equivalent document.

² In the Office Action, only the '128 DE Patent Publication was cited. The '617 US Patent is an equivalent document.

acknowledge consideration of this document. Since the document was previously before the Examiner and should have been considered, it is submitted that no substantial burden is now placed on the Examiner to acknowledge consideration of this document.

Initially, under cover of this Response, the Applicants submit marked-up and substitute specifications. The marked-up specification contains the changes the Applicants propose making to the specification as filed. These changes include the amendments to place certain information in SI units as requested in the Office Action. Additional amendments are made to place the application in a more idiomatic form of English and to insert the section headings preferred under the USPTO's Rules Of Practice. The proposed changes are entered onto the substitute specification. The undersigned registered representative hereby states that the substitute specification does not contain any new matter different from what was in the application when filed.

In the Office Action, objections were lodged against the Abstract. A revised Abstract is provided.

Claims 10, 15 and 16 are canceled. New Claims 19-35 are added. Claims 11-14, 17 and 18 are amended. Claims 19 and 25 are the independent claims of this application. Claims 11-14, 17, 18 and 20-24 are dependent from Claim 19. Claims 26-35 are dependent from Claim 25.

Miyazaki is directed to a gas analyzing apparatus that measures the absorption of a single beam of radiation to measure the ingredient of the sample.

When the gas analyzing apparatus measures concentrations of a plurality of ingredients in the sample gas, it preferably has at least two detection means. . .³

³ U.S. Patent No. 5,689,114, column 1, lines 61-64.

Specifically, Miyazaki discloses a detection assembly with a chamber 38 through which two luminous fluxes L1 and L2, respectively are directed. Luminous flux L1 is directed to a first detector 10a. Luminous flux L2 is directed to a second detector 10b.

In order to make these measurements, detector 10a "has a sensitivity only to the infrared luminous flux having a wavelength identical to the wavelength inherent in the $^{13}\text{CO}_2$ gas."⁴ Detector 10b "has a sensitivity only to the infrared luminous flux having a wavelength identical to the wavelength inherent in the $^{13}\text{CO}_2$ gas."⁵

Burch similarly is directed to a "non-dispersive gas analyzer to evaluate a plurality of gas species in a sample."⁶ Burch's analyzer is provided with two photodetectors 41 and 46. Burch goes on to state that,

In operation selector cell 20 is filled with two different gas species at two separated wavelengths. . . Filter 47 selectively [passes the] wavelength associated with the absorption spectra of one gas [to photodetector 46]. Filter 40 selectively [passes the] wavelength associated with the absorption spectra of the other gas [to photodetector 41]. . . The output of the two photodetectors 41 and 46 will contain modulation products related to their corresponding gas species in sample cell 34. (*Emphasis Added*)⁷

Thus, both Miyazaki and Burch are directed to equipment wherein dual radiation beams are monitored by detectors responsive to different wavelengths in order to simultaneously measure two components in a specimen.

Even when combined, the sum of these documents does not equal Applicants' invention of Claims 19 and 25 wherein a pair of detectors are provided that each measure radiation at the same wavelength, namely the wavelength at which the substance

⁴ U.S. Patent No. 5,689,114, column 7, lines 31-34.

⁵ U.S. Patent No. 5,689,114, column 7, lines 36-39.

⁶ U.S. Patent No. 3,916,195, column 1, lines 33-35.

⁷ U.S. Patent No. 3,916,195, column 5, lines 8-25.

being tested for absorbs radiation. This difference is further emphasized by dependent Claims 22 and 33. The claims recite that, in order to measure for a second substance a second pair of receivers is provided.

The claimed system of the present application is used to measure the concentration of a substance under test by comparing the relative absorption of the radiation over two beams paths of different length. In the arrangement of this invention, the mirrors that reflect the radiation can be formed out of the same piece of material.⁸ Thus, the mirrors are subject to common changes in reflectivity due to such events as ageing or thermal expansion/contraction. These common changes in reflectivity are inherently factored out in the equations used to calculate substance combination so as to have no effect on the accuracy of the measurements made by the apparatus.

Moreover, even in he version of the invention recited by Claims 19 and 25, the resultant concentration determination is also independent of any spectral distributions changes of the radiation source.

Thus, the primary references, even when combined, do not equal an assembly having the features, the function or the advantages of Applicants' invention as recited by Claims 19 and 25.

Hagen merely teaches one how to construct an infrared radiator. Peters and Hirayama simply disclose assemblies with single mirrors. Thus, the secondary references are no more relevant to Applicants' invention than the above-discussed primary references.

The dependent claims are all allowable at least because they depend from allowable independent claims.

⁸ Claims 16, 17, 20, 21, 23 and 25-35 are directed to this version of the invention.

Moreover, Claims 16, 17, 20, 21, 23 and 25-35 are further directed to the version of the invention wherein the mirrors are formed from a single piece of material. As discussed above, an advantage of this version of the invention is that any changes of the mirrors due to thermal expansion/contraction or aging occur at the same rate to both mirrors. Thus, these changes in reflectivity have no affect on the measurements made by the assembly of this invention.

Therefore, at least the above-discussed dependent claims are further in condition for allowance because they are independently directed to an invention entitled to patent protection.

In sum, it is submitted that each claim of this application is directed to a patentable invention and is in an allowable form, since the claims, as well as the other parts of this application are in an allowable state, the Applicants now courteously solicit prompt issuance of a Notice Of Allowance.

Respectfully submitted,

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ANALYSIS APPARATUS

FIELD OF THE INVENTION

This invention relates to an analyzer for determining the concentration of one or more substances in a mixture by measuring the concentration-dependent molecule-specific extinction according to the preamble of claim 1.

BACKGROUND OF THE INVENTION

Nondispersive photometers for determining the concentration of a substance in a mixture are widely known and used for a great variety of measuring tasks. Thus, commercial medical measuring instruments for determining CO₂ content in tidal air, so-called capnometers, are based on this principle. Said These devices evaluate the attenuation of introduced infrared radiation at the wavelength of 4.26 microns micrometers characteristic of CO₂ according to Lambert-Beer's law

I = I₀ exp [-kCL]
where I: Detected intensity
 I₀: Irradiated intensity
 k: Specific extinction coefficient
 C: Concentration
 L: Optical path length

as a measure of the CO₂ concentration present in the sample.

In the simplest form, nondispersive photometers work according to a single-beam method (ef. See EP 0 794 423 A1).

IR radiation whose having an intensity is assumed to be constant is passed from a radiation source through the

volume penetrated by the sample under testing and measured therebehind for its intensity using. The measurement is performed using an optoelectric detector as a radiation receiver. The selectivity for the substance to be detected is ensured by restricting the IR spectrum to the characteristic wavelength(s) by a narrow-band filter disposed either behind the radiator or in front of the receiver.

Alternatively, unfiltered light is passed behind the absorption chamber in a closed chamber filled with the substance to be determined, in which chamber the radiant energy of the radiation source attenuated at the characteristic wavelength(s) in accordance with the concentration present in the absorption chamber is converted into thermal energy by optical excitation at exactly the characteristic wavelength(s) and detected as pressure (optopneumatic detector).

In order to obtain the signal-to-noise ratio required for the necessary measuring accuracy, periodic modulation of the signal is imperative. This is classically effected by the use of rotating beam chopping disks, so-called choppers. Since these are mechanically moving parts, this solution has inherent disadvantages with respect to minimum attainable size, interference susceptibility due to the action of external force, and perturbing effects such as vibrations or sound caused by the rotation. In modern devices one therefore uses compact, thermal thin-film or thick-film radiation sources which are operated with clocked current and thus emit periodically modulated radiation themselves.

The single-beam method with one radiation source and one receiver is hardly applied, however, since seldom employed. This is because temperature and intensity fluctuations and aging phenomena of the radiation source,

optical elements and receiver lead to strong drift of the output signal. In order to compensate ~~said~~for these effects, one usually employs a double-beam method which uses a second radiation path not influenced by the substance to be measured as a reference. The signals of the first (measuring) and second (reference) radiation paths are ratioed. ~~and the~~The ratio is used for determining the concentration.

Double-beam methods by which the radiation from the radiation source is split into measuring and reference radiation paths to two receivers can be realized with optical devices differing in the number of radiation sources, cells and/or receivers. A device with two radiation sources, one cell and two receivers is described e.g. in US 3,734,631. Compensation of thermal and aging effects in the cell is intrinsic to the method. Moreover, considerable measuring and automatic-control effort is necessary for keeping the radiant power of the two radiation sources constant, for instance by using two additional receivers for measuring the radiant power emitted by the radiation sources before the cell is traversed. A simplification of this assembly in that both radiation paths are passed onto one receiver is described in US 4,899,053. However, no stabilization of the intensities of the two radiation sources is provided.

Intensity fluctuations due to temperature fluctuations or signs of aging of the radiation source can be compensated intrinsically if both radiation paths, i.e. the reference and measuring radiation paths, are operated from the same radiation source. For this purpose one must perform beam splitting which is typically realized by prisms or semitransparent, partially dichroic mirrors in front of or behind the absorption chamber (~~ef.~~See EP 0 834 732 A2).

However, such optical components reduce intensity, which reduces the signal-to-noise ratio and thus worsens the lower detection limit. Furthermore, the spectral properties of such elements can change in the course of time through deposits or attack by aggressive media, which can lead to a shift of the intensity ratio between measuring and reference paths.

Advantageous beam splitting via imaging mirrors within the sample chamber doing without intensity-attenuating elements is described in DE 44 37 188 C2. The central requirement for the reference path is that its intensity not be influenced, or influenced substantially less than the measuring path, by concentration changes in the substance to be measured. For this purpose the reference path is guided almost completely through a transparent block of calcium fluoride in the interior of which there is no attenuation of light by the substance to be measured. However, such a block can cloud in the course of time through attack by aggressive media. More-over, exact adjustment of the mirrors and thus an elaborate adjusting device is necessary. Also, the adjustable mirrors form gaps and similar cavities which delay the exchange of the substance to be measured and thus lead to memory effects.

According to EP 0 780 681 A2, the reference beam traverses a reference cell filled with reference gas, but this involves the above-described disadvantages of prismatic beam splitting. Furthermore, it does not permit changes in the optical properties of the measuring cell to be detected. The miniaturization of such assemblies is limited.

Alternatively, measuring and reference beams are both guided through the measuring cell but measured in different wave ranges. The reference beam is either

measured in such broadband fashion that the intensity change through extinction at the characteristic wavelengths of the substance to be measured is irrelevant, or it is measured in narrow-fashion band like the measuring beam but at another wavelength. The disadvantage of the first method is that a change in spectral distribution of the radiation source due to temperature fluctuations or signs of aging will generally influence measuring and reference signals differently. The disadvantage of the second method is the uncertainty about the nonoccurrence of absorption at the reference wavelength due to unknown substances. This is dangerous specifically in the case of ~~ambient~~^{ambient} air monitoring for toxic gases since absorption at the reference wavelength leads to a reduction of sensitivity in the measuring path.

According to US 4,281,248 the radiation of an IR radiation source is supplied to optopneumatic detectors with a chopper alternatively via a reference radiation path and a measuring radiation path. The gas to be measured flows through a long cell in the measuring radiation path and then through a short cell in the reference radiation path.

According to US 5,876,674 the radiation of a radiation source is split into two radiation paths and the gas to be measured guided through an absorption chamber having in each radiation path two optical elements formed as aligned glass rods each at different distance so that the optical path length in the absorption chamber is greater between one pair of optical elements than with the other pair.

SUMMARY OF THE INVENTION

~~The invention is based on the problem of providing~~ object of the invention is to provide an analyzer for determining concentration by transmission measurement which is compact and stable toward outside mechanical and thermal influences and permits a wide concentration range - from a few ppm to several ten percent - to be determined reliably and continuously.

~~This is obtained according to the invention with the analyzer characterized in claim 1. The subclaims state advantageous embodiments of the inventive analyzer.~~

According to the invention, two radiation paths, i.e. a first radiation path from the radiation source to a first receiver and a second radiation path from the radiation source to a second receiver, traverse the absorption chamber containing the sample with the substance ~~whose~~ the concentration of which is to be determined.

In both radiation paths measuring is ~~done~~ performed at the same wavelength. However, the two radiation paths have ~~a~~ different lengthlengths, the fist being substantially longer than the second, preferably at least twice, in particular at least four times, as long. This causes the radiation passing along the first, long path to be attenuated ~~accordingly~~ more in the presence of the substance to be detected than the radiation along the second, shorter path.

In delimitation over the prior art, the two radiation paths are thus not only guided completely through the sample to be measured but are furthermore measured at the same wavelength. This results in optical equivalence of the two beams which avoids essential disadvantages of the approaches hitherto described. Due to the equivalent beam control, any intensity-attenuating

perturbing effects possibly occurring in the course of time act on both radiation paths to the same extent. Due to the measurement of both radiation paths at the same wavelength, the measuring result is independent of the spectral distribution of the radiation source, the spectral properties of the optical elements or changes thereof through aging effects since both radiation paths are influenced to the same extent ~~hereby these~~ factors.

The greatly different absorption paths in the two radiation paths furthermore permit the dynamic range of the device to be advantageously widened. If, at high concentrations of the substance to be measured, the absorption in the long radiation path is so strong that the signal arriving at the detector falls below the noise limit, the signal from the shorter radiation path can be evaluated directly. The attainable dynamic gain corresponds to the ratio of the two absorption paths.

From the radiation intensity measured by each receiver, one forms an intensity comparative value, for example the quotient of the intensities measured by the first and second receivers, ~~said~~ This measured intensity comparative value or intensity quotient ~~corresponding~~ corresponds to a certain concentration of the substance to be measured. If one applies Lambert-Beer's law as mentioned above to both radiation paths, forms the quotient of the two equations, takes the logarithm and solves for concentration, one obtains

$$C = -1 / (k L_1 - k L_2) \ln (I_1 / I_2)$$

On the other hand, one can first logarithmize the two equations, expand them accordingly, subtract from

each other and solve for irradiated intensity. One obtains

$$I_0 = \exp [L_1 \ln I_2 - L_2 \ln I_1 / (L_1 - L_2)]$$

Evaluation of the signals of both receivers thus permits not only the determination of concentration C but also a statement about irradiated power I_0 . Even if this value is for technical reasons not used for controlling the radiation source, it can be used for redundant functional testing of the analyzer.

The method can be performed not only in a single-channel fashion, i.e. for determining the concentration of a substance in a sample, but also in multi-channel fashion, i.e. for simultaneously determining the concentrations of a plurality of substances in a mixture. In the latter case one requires a pair of radiation paths, a first long one and a second short one, for each individual channel to be measured. However, the radiation paths of all channels are operated from the same radiation source and guided through the same sample according to the invention.

The inventive analyzer or photometer is applicable in particular for determining substances in gas mixtures. However, it can also be used to determine the concentration of a substance in a liquid.

Due to the monolithic assembly and the resulting high mechanical stability, the inventive analyzer is compression-proof and also helium-leakproof. It can accordingly be used for measurements in the pressure range from vacuum to ~~10~~ $\text{bar} \times 10^6$ Pascals for example.

As radiation one uses in particular infrared radiation. The infrared radiation source irradiates the sample to be analyzed and the receivers or detectors

measure the attenuation of the IR radiation. The selectivity for a certain substance is obtained by narrow-band filtering of the light to a range in which the substance absorbs IR radiation as greatly as possible in a characteristic wave range through molecule vibrations.

As an IR radiation source one preferably uses a thermal IR radiation source; one also preferably uses thermal receivers, e.g. pyrodetectors or thermopiles. However, it is also possible to use alternative electrooptical radiation sources such as diode lasers which work at low temperatures, or gas lasers. As receivers one can also use quantum detectors.

To form the two optical paths of different lengths belonging to a channel in the absorption chamber one preferably provides two mirrors in the absorption chamber which are disposed at different distances from the IR radiation source and reflect radiation of the radiation source onto first and second receivers.

The mirrors are preferably formed according to the invention by concave mirrors, whereby one preferably uses aspheric mirrors, in particular mirrors whose surface is formed by a section of a spheroid. Thus the light emitted by the radiation source is focused almost completely onto the receivers.

As a radiation source one therefore uses according to the invention an IR plane radiator produced by the thin- or thick-film technique. Since plane radiators have an angular distribution of emission following the law of cosines and thus emit a strongly forward directed radiation in contrast to point or line radiators, their radiation can be focused especially advantageously onto the receivers. In order to be protected from aging through gas contact or destruction upon measurement of

reactive gases, the radiation source is preferably disposed outside the absorption chamber, i.e., separated gastight by an optical window from the absorption chamber and thus the substance to be measured.

The filter for filtering out the wave range of IR radiation characteristic of the substance to be measured can be disposed on the radiation source or both receivers in the case of single-channel measurement. In the case of multi-channel measurement the filters must be mounted in front of the receivers.

If the filters are mounted in front of the receivers, they must have pairwise exactly identical optical properties. In order to avoid differences in optical properties, as occur for production reasons both between different batches of filter material and due to inhomogeneities on one and the same disk of a filter, the filters belonging to a channel are especially advantageously cut out of adjacent areas of one and the same filter disk.

The inventive analyzer preferably has a monolithic assembly. That is, the mirrors are formed integrally with the housing whose interior forms the absorption chamber. For integral formation with the housing, the mirrors can be produced by machining the inside of the housing, forming the mirrors when casting the housing or the like. One can thus also do without installation of the mirrors and adjustment of the mirrors.

So that the interior of the housing is accessible, the housing is preferably partite. The mirrors are then preferably formed integrally with the same housing part. Due to this monolithic assembly one also requires few seals.

Since the interior of the housing at the same time forms the absorption chamber there are no separating

surfaces, dead volumes or mountings between housing and mirrors, absorption chamber and housing, etc., with the monolithic design of the inventive analyzer. One thus obtains not only fast media exchange without memory effects but also reliably maintains the imaging geometry of the inventive device in case of temperature changes or mechanical influences.

The integral formation of the mirrors with the housing or the one housing part on which they are provided results in first-order compensation of thermal expansions upon temperature changes which would lead to a change of the lengths of the two optical paths belonging to a channel relative to each other. At the same time, the integral formation of the mirrors with the housing or the one housing part obtains high mechanical stability and thus effectively prevents a signal change due to outside mechanical influences.

The housing is preferably made of metal. This ensures not only high stiffness and thus high mechanical stability but also fast temperature compensation, in particular through metals high thermal conductivity and low heat capacity in order to ensure a fast temperature balance.

Suitable metals have proved to be in particular aluminum materials, i.e. aluminum metal or aluminum alloys, in particular temper annealed metal or aluminum materials, in order to prevent slow drift through internal stresses and thereby ensure high long-term stability.

Apart from that, aluminum materials permit the mirrors to be easily worked out for example by machining. Moreover, mirror surfaces of aluminum materials have high IR reflectivity. Mirror surfaces of aluminum materials are also inert to most media or they form a corrosion-

inhibiting protective layer, for example toward oxygen (air) or fluorine-containing compounds through Al_2O_3 or AlF_3 protective layer. This layer is generally so thin that the optical properties are not influenced.

A metal housing moreover ensures an electric and magnetic shielding, which is important in particular for very small signals. The electronic housing receiving the devices for signal processing can be fastened to the photometer housing with the absorption chamber, the radiation source, the two receivers and the two mirrors, thereby ensuring good shielding for the total signal path. The electronic housing is for this purpose preferably made of the same material as the photometer housing, also in order to prevent temperature stresses due to different temperature expansion coefficients.

The radiation of the radiation source is preferably modulated in order to be independent of background radiation on the receiver side. If one wants to do without mechanically moving parts (choppers), the radiation source must be designed so as to be electrically modulated.

The inventive analyzer can be used for example for analyzing environmentally harmful or toxic gas, in particular for continuous monitoring of waste gases, for example for monitoring waste-gas cleaning installations. Environmentally harmful gases which can be analyzed with the inventive device are in particular inert, fluorine-containing gases, for example fluorinated or perfluorinated hydrocarbons, nitrogen trifluoride or sulfur hexafluoride.

With the inventive device one can reliably and continuously determine the concentration of one or more substances of e.g. less than 1 ppm to 50% and more.

BRIEF DESCRIPTION OF THE DRAWINGS

In the following description, a single-channel embodiment and a double-channel embodiment of the inventive analyzer will be explained in more detail by way of example with reference to the drawings, in which:

FIG. 1 shows schematically a view of the radiation path of the device;

FIGS. 2a and 2b show perspective views of the two housing half-members of the double-channel device in the open state; and

FIGS. 3a and 3b show perspective views of the two housing half-members of the double-channel device in the open state.

DETAILED DESCRIPTION

The device accordingly has two housing parts 1, 2 of substantially equal size indicated by dashed lines in FIG. 1.

According to FIG. 2, housing half-members 1, 2 are of substantially cuboid form, for example made of an aluminum material. Between housing half-members 1, 2 there is sealing ring 3. Bores 4, 5 are for screwing housing half-members 1, 2 together.

A cavity is worked out of inside 6 of housing half-member 2 to form concave mirror 7. Further, A projection 8 is worked out of inside 6 of housing half-member 2, and smaller second concave mirror 9 at the tip of projection 8. First concave mirror 7 is disposed at a substantially greater distance from IR radiation source 11 than second concave mirror 9. Concave mirrors 7, 9 integral with housing part 2 each form sections of a spheroid, the axes The diameter of the spheroid of first concave mirror 7 being accordingly greater than the axes diameter of the spheroid of second concave mirror 9. The two

~~sphereids~~ Mirrors 7 and 9 are ~~so disposed~~ positioned so that the radiation source and one of the receivers are located at the focal points in each case. Inside 12 of housing part 1 likewise has a cavity for receiving projection 8, among other things.

The cavities on insides 6, 12 of housing parts 2, 1 form absorption chamber 13 of the mounted housing (FIG. 1).

The medium to be analyzed is supplied to absorption chamber 13 via bore 14 in the wall of housing part 2 which is opposite mirror 7 (FIG. 2b). The medium exits through another bore (not shown) in housing part 1 or 2.

IR radiation source 11, formed as a plane radiator, is disposed outside housing part 1 ~~en~~ and ~~seats in an~~ opening 16. Further, first receiver 17 is provided ~~enseated in~~ opening 18 and second receiver 19 ~~en~~ ~~another~~ ~~is seated in~~ opening 21 in housing part 1 (FIG. 2).

According to FIG. 1, radiation from radiation source 11 is split on the edge of mirror 9 facing mirror 7 into radiation paths 22 and 23, preferably and especially advantageously in equal shares. Radiation paths 22, 23 from radiation source 11 to receivers 17, 19 traverse absorption chamber 13 and thus the substance to be analyzed contained therein. The one radiation path 22 by which part of the radiation from the radiation source is reflected by large mirror 7 has a substantially greater length than radiation path 22 with reflection on other mirror 9.

The double-channel configuration shown in FIG. 3a/b ~~Figures 3a and 3b~~ differs from the single-channel configuration shown in FIG. 2a/b ~~Figures 2a and 2b~~ only in the number of receivers and the formation of the mirrors. Instead of the single receivers in housing openings 18

and 21 in the single-channel configuration, one inserts two receivers in each case into housing openings 18 and 21, 18a and 21a (FIG. 3a) here. In the double-channel configuration, mirrors 7 and 9 of the single-channel configuration are broken in the plane shown in FIG. 1 and tilted away orthogonally therefrom such that the radiation source in housing opening 16 and the receivers in openings 18 and 21, 18a and 21a are seated at the focal points of mirrors 7 and 9, 7a and 9a in each case (FIG. 3b).

What is claimed is:

ANALYSIS APPARATUS

FIELD OF THE INVENTION

This invention relates to an analyzer for determining the concentration of one or more substances in a mixture by measuring the concentration-dependent molecule-specific extinction.

BACKGROUND OF THE INVENTION

Nondispersive photometers for determining the concentration of a substance in a mixture are widely known and used for a great variety of measuring tasks. Thus, commercial medical measuring instruments for determining CO₂ content in tidal air, so-called capnometers, are based on this principle. These devices evaluate the attenuation of introduced infrared radiation at the wavelength of 4.26 micrometers characteristic of CO₂ according to Lambert-Beer's law

$$I = I_0 \exp [-kCL]$$

where I: Detected intensity
 I₀: Irradiated intensity
 k: Specific extinction coefficient
 C: Concentration
 L: Optical path length

as a measure of the CO₂ concentration present in the sample.

In the simplest form, nondispersive photometers work according to a single-beam method (See EP 0 794 423 A1).

IR radiation having an intensity assumed to be constant is passed from a radiation source through the volume penetrated by the sample under testing and measured therebehind for its intensity. The measurement

is performed using an optoelectric detector as a radiation receiver. The selectivity for the substance to be detected is ensured by restricting the IR spectrum to the characteristic wavelength(s) by a narrow-band filter disposed either behind the radiator or in front of the receiver.

Alternatively, unfiltered light is passed behind the absorption chamber in a closed chamber filled with the substance to be determined, in which chamber the radiant energy of the radiation source attenuated at the characteristic wavelength(s) in accordance with the concentration present in the absorption chamber is converted into thermal energy by optical excitation at exactly the characteristic wavelength(s) and detected as pressure (optopneumatic detector).

In order to obtain the signal-to-noise ratio required for the necessary measuring accuracy, periodic modulation of the signal is imperative. This is classically effected by the use of rotating beam chopping disks, so-called choppers. Since these are mechanically moving parts, this solution has inherent disadvantages with respect to minimum attainable size, interference susceptibility due to the action of external force, and perturbing effects such as vibrations or sound caused by the rotation. In modern devices one therefore uses compact, thermal thin-film or thick-film radiation sources which are operated with clocked current and thus emit periodically modulated radiation themselves.

The single-beam method with one radiation source and one receiver is seldom employed. This is because temperature and intensity fluctuations and aging phenomena of the radiation source, optical elements and receiver lead to strong drift of the output signal. In order to compensate for these effects, one usually

employs a double-beam method which uses a second radiation path not influenced by the substance to be measured as a reference. The signals of the first (measuring) and second (reference) radiation paths are ratioed. The ratio is used for determining the concentration.

Double-beam methods by which the radiation from the radiation source is split into measuring and reference radiation paths to two receivers can be realized with optical devices differing in the number of radiation sources, cells and/or receivers. A device with two radiation sources, one cell and two receivers is described in US 3,734,631. Compensation of thermal and aging effects in the cell is intrinsic to the method. Moreover, considerable measuring and automatic-control effort is necessary for keeping the radiant power of the two radiation sources constant, for instance by using two additional receivers for measuring the radiant power emitted by the radiation sources before the cell is traversed. A simplification of this assembly in that both radiation paths are passed onto one receiver is described in US 4,899,053. However, no stabilization of the intensities of the two radiation sources is provided.

Intensity fluctuations due to temperature fluctuations or signs of aging of the radiation source can be compensated intrinsically if both radiation paths, i.e. the reference and measuring radiation paths, are operated from the same radiation source. For this purpose one must perform beam splitting which is typically realized by prisms or semitransparent, partially dichroic mirrors in front of or behind the absorption chamber (See EP 0 834 732 A2).

However, such optical components reduce intensity, which reduces the signal-to-noise ratio and thus worsens

the lower detection limit. Furthermore, the spectral properties of such elements can change in the course of time through deposits or attack by aggressive media, which can lead to a shift of the intensity ratio between measuring and reference paths.

Advantageous beam splitting via imaging mirrors within the sample chamber doing without intensity-attenuating elements is described in DE 44 37 188 C2. The central requirement for the reference path is that its intensity not be influenced, or influenced substantially less than the measuring path, by concentration changes in the substance to be measured. For this purpose the reference path is guided almost completely through a transparent block of calcium fluoride in the interior of which there is no attenuation of light by the substance to be measured. However, such a block can cloud in the course of time through attack by aggressive media. More-over, exact adjustment of the mirrors and thus an elaborate adjusting device is necessary. Also, the adjustable mirrors form gaps and similar cavities which delay the exchange of the substance to be measured and thus lead to memory effects.

According to EP 0 780 681 A2, the reference beam traverses a reference cell filled with reference gas, but this involves the above-described disadvantages of prismatic beam splitting. Furthermore, it does not permit changes in the optical properties of the measuring cell to be detected. The miniaturization of such assemblies is limited.

Alternatively, measuring and reference beams are both guided through the measuring cell but measured in different wave ranges. The reference beam is either measured in such broadband fashion that the intensity change through extinction at the characteristic

wavelengths of the substance to be measured is irrelevant, or it is measured in narrow-fashion band like the measuring beam but at another wavelength. The disadvantage of the first method is that a change in spectral distribution of the radiation source due to temperature fluctuations or signs of aging will generally influence measuring and reference signals differently. The disadvantage of the second method is the uncertainty about the nonoccurrence of absorption at the reference wavelength due to unknown substances. This is dangerous specifically in the case of ambient air monitoring for toxic gases since absorption at the reference wavelength leads to a reduction of sensitivity in the measuring path.

According to US 4,281,248 the radiation of an IR radiation source is supplied to optopneumatic detectors with a chopper alternatively via a reference radiation path and a measuring radiation path. The gas to be measured flows through a long cell in the measuring radiation path and then through a short cell in the reference radiation path.

According to US 5,876,674 the radiation of a radiation source is split into two radiation paths and the gas to be measured guided through an absorption chamber having in each radiation path two optical elements formed as aligned glass rods each at different distance so that the optical path length in the absorption chamber is greater between one pair of optical elements than with the other pair.

SUMMARY OF THE INVENTION

The object of the invention is to provide an analyzer for determining concentration by transmission measurement which is compact and stable toward outside mechanical and thermal influences and permits a wide concentration range - from a few ppm to several ten percent - to be determined reliably and continuously.

According to the invention, two radiation paths, i.e. a first radiation path from the radiation source to a first receiver and a second radiation path from the radiation source to a second receiver, traverse the absorption chamber containing the sample with the substance the concentration of which is to be determined.

In both radiation paths measuring is performed at the same wavelength. However, the two radiation paths have different lengths, the first being substantially longer than the second, preferably at least twice, in particular at least four times, as long. This causes the radiation passing along the first, long path to be attenuated more in the presence of the substance to be detected than the radiation along the second, shorter path.

In delimitation over the prior art, the two radiation paths are thus not only guided completely through the sample to be measured but are furthermore measured at the same wavelength. This results in optical equivalence of the two beams which avoids essential disadvantages of the approaches hitherto described. Due to the equivalent beam control, any intensity-attenuating perturbing effects possibly occurring in the course of time act on both radiation paths to the same extent. Due to the measurement of both radiation paths at the same wavelength, the measuring result is independent of the

spectral distribution of the radiation source, the spectral properties of the optical elements or changes thereof through aging effects since both radiation paths are influenced to the same extent by these factors.

The greatly different absorption paths in the two radiation paths furthermore permit the dynamic range of the device to be advantageously widened. If, at high concentrations of the substance to be measured, the absorption in the long radiation path is so strong that the signal arriving at the detector falls below the noise limit, the signal from the shorter radiation path can be evaluated directly. The attainable dynamic gain corresponds to the ratio of the two absorption paths.

From the radiation intensity measured by each receiver, one forms an intensity comparative value, for example the quotient of the intensities measured by the first and second receivers. This measured intensity comparative value or intensity quotient corresponds to a certain concentration of the substance to be measured. If one applies Lambert-Beer's law as mentioned above to both radiation paths, forms the quotient of the two equations, takes the logarithm and solves for concentration, one obtains

$$C = -1 / (k L_1 - k L_2) \ln (I_1 / I_2)$$

On the other hand, one can first logarithmize the two equations, expand them accordingly, subtract from each other and solve for irradiated intensity. One obtains

$$I_0 = \exp [L_1 \ln I_2 - L_2 \ln I_1 / (L_1 - L_2)]$$

Evaluation of the signals of both receivers thus permits not only the determination of concentration C but also a statement about irradiated power I_0 . Even if this value is for technical reasons not used for controlling the radiation source, it can be used for redundant functional testing of the analyzer.

The method can be performed not only in a single-channel fashion, i.e. for determining the concentration of a substance in a sample, but also in multi-channel fashion, i.e. for simultaneously determining the concentrations of a plurality of substances in a mixture. In the latter case one requires a pair of radiation paths, a first long one and a second short one, for each individual channel to be measured. However, the radiation paths of all channels are operated from the same radiation source and guided through the same sample according to the invention.

The inventive analyzer or photometer is applicable in particular for determining substances in gas mixtures. However, it can also be used to determine the concentration of a substance in a liquid.

Due to the monolithic assembly and the resulting high mechanical stability, the inventive analyzer is compression-proof and also helium-leakproof. It can accordingly be used for measurements in the pressure range from vacuum to 10^6 Pascals for example.

As radiation one uses in particular infrared radiation. The infrared radiation source irradiates the sample to be analyzed and the receivers or detectors measure the attenuation of the IR radiation. The selectivity for a certain substance is obtained by narrow-band filtering of the light to a range in which the substance absorbs IR radiation as greatly as possible

in a characteristic wave range through molecule vibrations.

As an IR radiation source one preferably uses a thermal IR radiation source; one also preferably uses thermal receivers, e.g. pyrodetectors or thermopiles. However, it is also possible to use alternative electrooptical radiation sources such as diode lasers which work at low temperatures, or gas lasers. As receivers one can also use quantum detectors.

To form the two optical paths of different lengths belonging to a channel in the absorption chamber one preferably provides two mirrors in the absorption chamber which are disposed at different distances from the IR radiation source and reflect radiation of the radiation source onto first and second receivers.

The mirrors are preferably formed according to the invention by concave mirrors, whereby one preferably uses aspheric mirrors, in particular mirrors whose surface is formed by a section of a spheroid. Thus the light emitted by the radiation source is focused almost completely onto the receivers.

As a radiation source one therefore uses according to the invention an IR plane radiator produced by the thin- or thick-film technique. Since plane radiators have an angular distribution of emission following the law of cosines and thus emit a strongly forward directed radiation in contrast to point or line radiators, their radiation can be focused especially advantageously onto the receivers. In order to be protected from aging through gas contact or destruction upon measurement of reactive gases, the radiation source is preferably disposed outside the absorption chamber, i.e., separated gastight by an optical window from the absorption chamber and thus the substance to be measured.

The filter for filtering out the wave range of IR radiation characteristic of the substance to be measured can be disposed on the radiation source or both receivers in the case of single-channel measurement. In the case of multi-channel measurement the filters must be mounted in front of the receivers.

If the filters are mounted in front of the receivers, they must have pairwise exactly identical optical properties. In order to avoid differences in optical properties, as occur for production reasons both between different batches of filter material and due to inhomogeneities on one and the same disk of a filter, the filters belonging to a channel are especially advantageously cut out of adjacent areas of one and the same filter disk.

The inventive analyzer preferably has a monolithic assembly. That is, the mirrors are formed integrally with the housing whose interior forms the absorption chamber. For integral formation with the housing, the mirrors can be produced by machining the inside of the housing, forming the mirrors when casting the housing or the like. One can thus also do without installation of the mirrors and adjustment of the mirrors.

So that the interior of the housing is accessible, the housing is preferably partite. The mirrors are then preferably formed integrally with the same housing part. Due to this monolithic assembly one also requires few seals.

Since the interior of the housing at the same time forms the absorption chamber there are no separating surfaces, dead volumes or mountings between housing and mirrors, absorption chamber and housing, etc., with the monolithic design of the inventive analyzer. One thus obtains not only fast media exchange without memory

effects but also reliably maintains the imaging geometry of the inventive device in case of temperature changes or mechanical influences.

The integral formation of the mirrors with the housing or the one housing part on which they are provided results in first-order compensation of thermal expansions upon temperature changes which would lead to a change of the lengths of the two optical paths belonging to a channel relative to each other. At the same time, the integral formation of the mirrors with the housing or the one housing part obtains high mechanical stability and thus effectively prevents a signal change due to outside mechanical influences.

The housing is preferably made of metal. This ensures not only high stiffness and thus high mechanical stability but also fast temperature compensation, in particular through metals high thermal conductivity and low heat capacity in order to ensure a fast temperature balance.

Suitable metals have proved to be in particular aluminum materials, i.e. aluminum metal or aluminum alloys, in particular temper annealed metal or aluminum materials, in order to prevent slow drift through internal stresses and thereby ensure high long-term stability.

Apart from that, aluminum materials permit the mirrors to be easily worked out for example by machining. Moreover, mirror surfaces of aluminum materials have high IR reflectivity. Mirror surfaces of aluminum materials are also inert to most media or they form a corrosion-inhibiting protective layer, for example toward oxygen (air) or fluorine-containing compounds through Al_2O_3 or AlF_3 protective layer. This layer is generally so thin that the optical properties are not influenced.

A metal housing moreover ensures an electric and magnetic shielding, which is important in particular for very small signals. The electronic housing receiving the devices for signal processing can be fastened to the photometer housing with the absorption chamber, the radiation source, the two receivers and the two mirrors, thereby ensuring good shielding for the total signal path. The electronic housing is for this purpose preferably made of the same material as the photometer housing, also in order to prevent temperature stresses due to different temperature expansion coefficients.

The radiation of the radiation source is preferably modulated in order to be independent of background radiation on the receiver side. If one wants to do without mechanically moving parts (choppers), the radiation source must be designed so as to be electrically modulated.

The inventive analyzer can be used for example for analyzing environmentally harmful or toxic gas, in particular for continuous monitoring of waste gases, for example for monitoring waste-gas cleaning installations. Environmentally harmful gases which can be analyzed with the inventive device are in particular inert, fluorine-containing gases, for example fluorinated or perfluorinated hydrocarbons, nitrogen trifluoride or sulfur hexafluoride.

With the inventive device one can reliably and continuously determine the concentration of one or more substances of e.g. less than 1 ppm to 50% and more.

BRIEF DESCRIPTION OF THE DRAWINGS

In the following description, a single-channel embodiment and a double-channel embodiment of the

inventive analyzer will be explained in more detail by way of example with reference to the drawings, in which:

FIG. 1 shows schematically a view of the radiation path of the device;

FIGS. 2a and 2b show perspective views of the two housing half-members of the double-channel device in the open state; and

FIGS. 3a and 3b show perspective views of the two housing half-members of the double-channel device in the open state.

DETAILED DESCRIPTION

The device accordingly has two housing parts 1, 2 of substantially equal size indicated by dashed lines in FIG. 1.

According to FIG. 2, housing half-members 1, 2 are of substantially cuboid form, for example made of an aluminum material. Between housing half-members 1, 2 there is sealing ring 3. Bores 4, 5 are for screwing housing half-members 1, 2 together.

A cavity is worked out of inside 6 of housing half-member 2 to form concave mirror 7. A projection 8 is worked out of inside 6 of housing half-member 2, and smaller second concave mirror 9 at the tip of projection 8. First concave mirror 7 is disposed at a substantially greater distance from IR radiation source 11 than second concave mirror 9. Concave mirrors 7, 9 integral with housing part 2 each form sections of a spheroid. The diameter of the spheroid of first concave mirror 7 being accordingly greater than the diameter of the spheroid of second concave mirror 9. Mirrors 7 and 9 are positioned so that the radiation source and one of the receivers are located at the focal points in each case. Inside 12 of

housing part 1 likewise has a cavity for receiving projection 8, among other things.

The cavities on insides 6, 12 of housing parts 2, 1 form absorption chamber 13 of the mounted housing (FIG. 1).

The medium to be analyzed is supplied to absorption chamber 13 via bore 14 in the wall of housing part 2 which is opposite mirror 7 (FIG. 2b). The medium exits through another bore (not shown) in housing part 1 or 2.

IR radiation source 11, formed as a plane radiator, is disposed outside housing part 1 and seats in an opening 16. Further, first receiver 17 is seated in opening 18 and second receiver 19 is seated in opening 21 in housing part 1 (FIG. 2).

According to FIG. 1, radiation from radiation source 11 is split on the edge of mirror 9 facing mirror 7 into radiation paths 22 and 23, preferably and especially advantageously in equal shares. Radiation paths 22, 23 from radiation source 11 to receivers 17, 19 traverse absorption chamber 13 and thus the substance to be analyzed contained therein. The one radiation path 22 by which part of the radiation from the radiation source is reflected by large mirror 7 has a substantially greater length than radiation path 22 with reflection on other mirror 9.

The double-channel configuration shown in Figures 3a and 3b differs from the single-channel configuration shown in Figures 2a and 2b only in the number of receivers and the formation of the mirrors. Instead of the single receivers in housing openings 18 and 21 in the single-channel configuration, one inserts two receivers in each case into housing openings 18 and 21, 18a and 21a (FIG. 3a) here. In the double-channel configuration, mirrors 7 and 9 of the single-channel configuration are

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broken in the plane shown in FIG. 1 and tilted away orthogonally therefrom such that the radiation source in housing opening 16 and the receivers in openings 18 and 21, 18a and 21a are seated at the focal points of mirrors 7 and 9, 7a and 9a in each case (FIG. 3b).

What is claimed is:

ANALYSIS APPARATUS

ABSTRACT

The invention relates to an analysis apparatus for determining the concentration of a substance in a mixture by measuring the concentration dependant molecule specific extinction of radiation in an absorption area (13) filled with the sample to be measured (13). Said apparatus has a radiation source (11) whose radiation is directed to two receivers (17, 19) and divided into corresponding radiation paths (22, 23), wherein the measuring value is formed by comparing the measured intensities of the receivers (17, 19). Both radiation paths (22, 23) from the radiation source (11) to the receivers (17, 19) pass through the substance in the absorption area (13) and have different lengths. An apparatus for measuring the concentration of a substance in a specimen. The apparatus includes a housing that defines a chamber for the specimen. A radiation source mounted to the housing emits radiation at a wavelength at which the radiation is absorbed by the substance. Two spaced apart receivers are mounted to the housing. Both receivers detect radiation at the wavelength at which it is absorbed by the specimen. Two concave mirrors are disposed in the housing. The mirrors are positioned to split the radiation emitted by the source into two beams, each of the beams being directed to a separate one of the receivers and so that the paths of travel of the beams from the source to the separate receivers are of different lengths. The concentration of the substance is determined by based on the difference in radiation detected by the receivers.